Bis(2-aminopyridine)(2,2′-bipyridine)-platinum(II) dinitrate dihydrate

Ken Sakai,* Norinobu Akiyama and Mina Mizota

Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162-8601, Japan

Correspondence e-mail:
ksakai@rs.kagu.tus.ac.jp

The Pt coordination plane in the title compound, $[Pt(C_{10}H_8N_2)(C_5H_6N_2)_2](NO_3)_2 \cdot 2H_2O$, is essentially planar and is nearly coplanar with the 2,2′-bipyridine (bpy) ligand. Two 2-aminopyridine ligands are bound to the Pt atom in a head-to-tail arrangement, and their planes are inclined with respect to the PtN$_4$ coordination plane by 74.4 (1) and 79.8 (1)°.

Comment

Multinuclear metal complexes have been considered as important mimics for catalyst surfaces. It is also known that many important biological processes at the active sites of enzymes often involve various metal complexes having more than two metal centers. In this context, we have been interested in di- and trinuclear systems involving effective metal–metal interactions (Sakai *et al.*, 1998), and we recently started exploring the coordination chemistry of platinum and 2-aminopyridine. Up to now, only five crystal structures have been reported for metal complexes with the 2-aminopyridine ligand, in which it serves as either a monodentate ligand (Krizanovic *et al.*, 1993; Xu *et al.*, 2000; Yip *et al.*, 2000) or a bridging ligand (Chakravarty *et al.*, 1984; Kanematsu *et al.*, 1999). The title compound, (I), has been prepared as a precursor for the development of new multinuclear systems. The subsequent synthetic studies, using (I), are now under way. This is the first example of a crystal structure of a platinum complex of 2-aminopyridine.

(I)
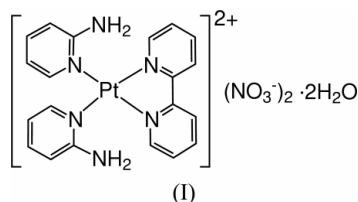
The Pt coordination plane is essentially planar (Fig. 1 and Table 1); the r.m.s. deviation of the four N atoms is negligibly small. The Pt atom is displaced from the coordination plane by 0.012 (2) Å. The bpy ligand has a slightly twisted geometry in which the two pyridyl planes are twisted at an angle of 2.0 (1)° to each other. The Pt coordination plane and the bpy plane are almost coplanar; the dihedral angle is only 0.80 (1)°. On the other hand, the pyridyl planes of the 2-aminopyridine ligands are steeply canted with respect to the Pt coordination plane, *viz.* 79.8 (1)° for the plane defined by N3/N4/C11–C15 and 74.4 (1)° for that by N5/N6/C16–C20.

An interesting feature is that one of the two nitrates has a strong π-stacking interaction with a part of the bpy moiety (Fig. 2); the plane-to-plane separation is *ca* 3.28 Å and the two
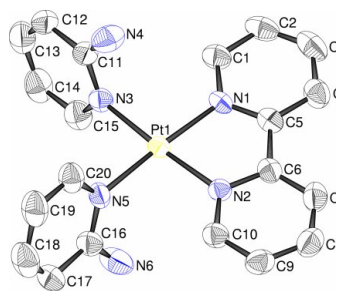
Figure 1
The structure of the cation of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.
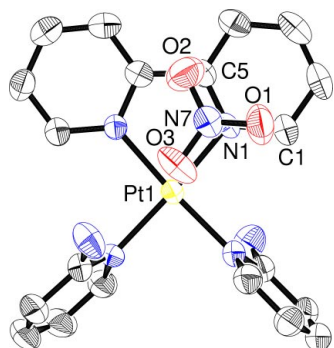

Figure 2
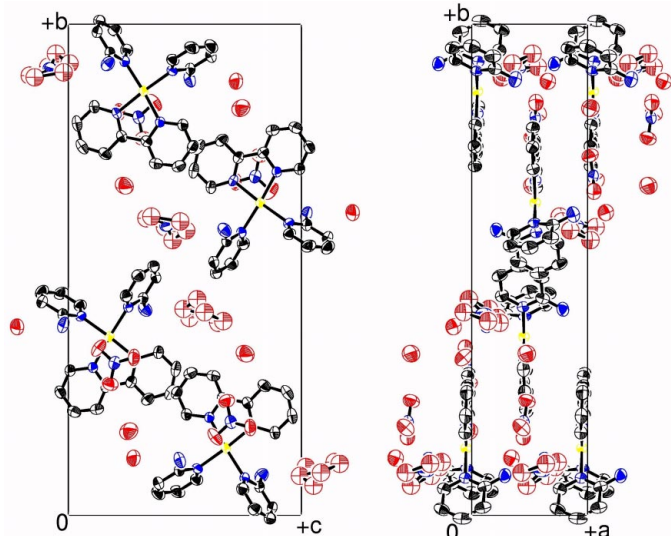A view showing a π-stack between the complex cation and a nitrate anion.

Figure 3
The crystal packing of (I), viewed along the a (left) and c axes (right).

planes are canted at an angle of 6.5 (2)°. The crystal packing is stabilized by weak π–π-stacking interactions (Fig. 3) and also by hydrogen-bonding interactions. The short $O \cdots O$ distances involving the water atoms O7 and O8 are listed in Table 1, and the $N-H \cdots O$ hydrogen-bonding geometry in Table 2.

Experimental

A solution of $PtCl_2(bpy)$ (1.0 mmol, 0.42 g; Morgan & Burstall, 1963), $AgNO_3$ (2.0 mmol, 0.34 g) and 2-aminopyridine (3.0 mmol, 0.28 g) in water (7 ml) was refluxed for 3 h. The solution was then filtered while it is hot to remove the precipitated AgCl. The dark purple filtrate was left in air at room temperature overnight. Pale-orange crystals were

deposited; they were collected by filtration and air-dried (yield, 35%). The compound was dissolved in water at 333 K (*ca* 0.1 g in 2 ml H_2O) followed by filtration if necessary. Allowing the filtrate to stand in air at room temperature overnight afforded the final product (I) as pale yellow needles (yield, 10%). Analysis calculated for $C_{20}H_{24}N_8O_8Pt$: C 34.34, H 3.46, N 16.02%; found: C 34.25, H 3.14, N 16.07%.

Crystal data

$[Pt(C_{10}H_8N_2)(C_5H_6N_2)_2](NO_3)_2 \cdot 2H_2O$	$D_x = 1.871$ Mg m^{-3}
$M_r = 699.56$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 8388 reflections
$a = 6.7374$ (3) Å	$\theta = 2.7$–28.0°
$b = 27.8864$ (13) Å	$\mu = 5.71$ mm^{-1}
$c = 13.5619$ (6) Å	$T = 296$ (2) K
$\beta = 102.876$ (1)°	Needle, pale yellow
$V = 2483.96$ (19) Å^3	$0.17 \times 0.12 \times 0.10$ mm
$Z = 4$	

Data collection

Bruker SMART APEX CCD-detector diffractometer	5573 independent reflections
	4451 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.098$
Absorption correction: Gaussian (*XPREP* in *SAINT*; Bruker, 2001)	$\theta_{max} = 28.2$°
	$h = -8 \rightarrow 8$
	$k = -34 \rightarrow 35$
$T_{min} = 0.147$, $T_{max} = 0.500$	$l = -12 \rightarrow 17$
15 077 measured reflections	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.038$	$w = 1/[\sigma^2(F_o^2) + (0.0327P)^2]$
$wR(F^2) = 0.083$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.95$	$(\Delta/\sigma)_{max} = 0.002$
5573 reflections	$\Delta\rho_{max} = 2.67$ e Å^{-3}
327 parameters	$\Delta\rho_{min} = -0.90$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pt1—N2	2.005 (4)	O7$\cdots$O6A^i	2.633 (11)
Pt1—N1	2.010 (4)	O7$\cdots$O8^{ii}	2.867 (8)
Pt1—N3	2.024 (4)	O7$\cdots$O6B^i	2.977 (15)
Pt1—N5	2.038 (4)	O8$\cdots$O6B^{iii}	2.824 (15)
O2$\cdots$O7	2.900 (8)	O8$\cdots$O4A^{iii}	2.955 (12)
N2—Pt1—N1	80.82 (16)	N2—Pt1—N5	95.31 (15)
N2—Pt1—N3	176.21 (15)	N1—Pt1—N5	176.07 (16)
N1—Pt1—N3	95.44 (16)	N3—Pt1—N5	88.42 (16)

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $x, y, z - 1$.

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N6—H6A$\cdots$O3	0.86	2.13	2.922 (6)	154
N6—H6B$\cdots$O8	0.86	2.10	2.926 (7)	160
N4—H4A$\cdots$O1^{iv}	0.86	2.24	3.013 (7)	150
N4—H4B$\cdots$O4B^{iv}	0.86	2.45	3.074 (14)	130
N4—H4B$\cdots$O5A^{iv}	0.86	2.15	2.926 (13)	150

Symmetry code: (iv) $1 + x, y, z$.

One of the two nitrate anions shows orientational disorder. Around the N8 atom there are two sets of possible positions of (O4A, O5A and O6A) and (O4B, O5B and O6B). It was assumed that these disordered O atoms have the same isotropic displacement parameter. Furthermore, the N—O distances were restrained at 1.22 Å, the three $O \cdots O$ distances within each NO_3 group were restrained as equal, and

each group was restrained to be planar. The occupation factors of sites *A* and *B* converged at 56.3 (8) and 43.7 (8)%, respectively. All H atoms, except those of the water molecules, were located at idealized positions as riding atoms (C—H = 0.93 Å for the aromatic rings and N—H = 0.86 Å for the amino groups). Water H atoms were not located. In the final difference Fourier synthesis, four residual peaks in the range 2.13–2.67 e Å^{-3} were observed within 0.88 Å from the Pt atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *KENX* (Sakai, 2002); software used to prepare material for publication: *SHELXL*97, *TEXSAN* (Molecular Structure Corporation, 2001), *KENX* and *ORTEP* (Johnson, 1976).

References

Bruker (2001). *SAINT* (Version 6.22) and *SMART* (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.

Chakravarty, A. R., Cotton, F. A. & Tocher, D. A. (1984). *Inorg. Chem.* **23**, 4030–4033.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kanematsu, N., Ebihara, M. & Kawamura, T. (1999). *Inorg. Chim. Acta*, **292**, 244–248.

Krizanovic, O., Sabat, M., Beyerle-Pfnur, R. & Lippert, B. (1993). *J. Am. Chem. Soc.* **115**, 5538–5548.

Molecular Structure Corporation (2001). *TEXSAN*. Version 1.11r1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Morgan, G. T. & Burstall, F. H. (1963). *J. Chem. Soc.* pp. 965–971.

Sakai, K. (2002). *KENX*. GUI for *SHELXL*97. Tokyo University of Science, Japan.

Sakai, K., Tanaka, Y., Tsuchiya, Y., Hirata, K., Tsubomura, T., Iijima, S. & Bhattacharjee, A. (1998). *J. Am. Chem. Soc.* **120**, 8366–8379.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Xu, Xingling., James, S. L., Mingos, D. M. P., White, A. J. P. & Williams, D. J. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3783–3790.

Yip, J. H. K., Suwarno & Vittal, J. J. (2000). *Inorg. Chem.* **39**, 3537–3543.